

REDUCTION OF COKE FORMATION DURING NAPHTHA PYROLYSIS

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by
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CERTIFICATE

This is to certify that the present work entitled "REDUCTION OF COKE FORMATION DURING NAPHTHA PYROLYSIS" by Kalyan Kumar Ghosh has been carried out under my supervision and has not been submitted elsewhere for a degree.

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Kalyan Kumar Ghosh
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NOMENCLATURE

C_A	Concentration of aromatics, kgmole/m^3
k_P	rate constant for coke formation on a surface completely covered with phosphorus complex
k_m	rate constant for coke formation in absence of phosphorus
k_S	rate constant for coke formation on a surface completely covered with sulphur complex
K_P	equilibrium constant for the phosphorus complex formation
K_S	equilibrium constant for sulphur complex
n	reaction order for coke formation reaction
P	phosphorus concentration, ppm/wt. fraction
r_a	asymptotic rate of coking, $\text{kg/m}^2\text{-h}$
r_{ap}	asymptotic rate of coking at $y_P=1$, $\text{kg/m}^2\text{-h}$
r_{ab}	asymptotic rate of coking at $y_P=0$, $\text{kg/m}^2\text{-h}$
y_P	fraction of metal surface covered with metal-phosphorus complex
y_S	fraction of metal surface covered with metal-sulphur complex
R	gas constant, $\text{J}/(\text{kmol})(\text{K})$
S	sulphur concentration, ppm/wt. fraction
T	temperature, K

Greek Symbols

δ	weight ratio of steam to naphtha, kg/kg
τ	space time, s

ABSTRACT

The reduction in the rate of coke formation during naphtha pyrolysis has been investigated in a jet-stirred reactor at atmospheric pressure in the temperature range 1078 to 1108 K. Reduction in coking rates was achieved either by coating the Inconel 600 metal with sodium silicate or by adding triethyl phosphite and/or thiophene to the feed. Rates of coke deposition were measured by periodically weighing a small metal plate suspended into the centre of the reactor.

Rates of coke formation were significantly reduced on sodium silicate coated surfaces. However, the rates of coke formation gradually increased with successive decokings of the coated surface. Addition of triethyl phosphite and/or thiophene to the naphtha also decreased the rate of coke formation by passivating the metal activity for coke formation. The addition of triethyl phosphite had no effect on the gas and liquid product yields.

A model has been proposed to account for the effect of temperature and phosphorus concentration on the rate of coke formation. This model can also be extended to account for the presence of sulphur in the feed.

CHAPTER 1

INTRODUCTION

Pyrolysis of hydrocarbons, such as ethane, propane and naphtha, to produce ethylene, propylene, butenes and butadienes, is an important petrochemical process. The pyrolysis operation involves heating the hydrocarbon, together with steam diluent, in radiantly heated coils to around 1100 K. A common problem associated with any pyrolysis process is the deposition of coke on the inner walls of the reactor and associated downstream heat exchangers. This undesirable coke, which can form to depths of several millimeters, reduces the heat transfer across the tube wall and also increases the pressure drop across the reactor. Thus, to maintain the same gas temperature profile and throughputs, the tube skin temperature and the reactor inlet pressure have to be increased as the run progresses. When the metal temperature reaches the limiting value, the reaction has to be shut down for decoking, by steam-air oxidation. Depending on the feed stock, the run lengths are limited from 4 to 8 weeks. Frequent decoking operation results in loss of production, increase the fuel and utility costs, and affect the coil life.

Although rates of coke formation during hydrocarbon pyrolysis have been investigated by several workers, very little attention has been focussed on finding methods to reduce the coke formation during pyrolysis. A common method of reducing coke formation during pyrolysis is either by addition of sulphur compounds to the feed or by presulphiding the reactor to form a passivating metal film. The disadvantage

of using sulphur to reduce coke formation is the resultant high level of sulphur in the product, which is undesirable. Catalytic gasification of coke during pyrolysis does not seem to be commercially viable since the catalytic effect of K_2CO_3 gradually decreases with the number of decokings (Mandal and Kunzru, 1986). Recently, it has been reported (Boone, 1983) that organic compounds containing phosphorus are very effective in reducing coke formation during naphtha pyrolysis. However, due to proprietary reasons the names of these compounds have not been revealed. Furthermore, in a Russian patent (Neberezhnova, 1982) it has been reported that organophosphorus compounds were effective in reducing coke formation during pyrolysis of liquid hydrocarbons.

The objective of the present investigation was to develop methods of reducing coke formation during naphtha pyrolysis. The effect of passivating the reactor metal surface with Na_2SiO_3 or adding triethyl phosphite to the naphtha feed on the rate of coke formation during naphtha pyrolysis was investigated. In addition, the effect of reactor temperature, the inlet hydrocarbon partial pressure and phosphorus content of the feed on the rate of coking has been studied. Another objective was to model the rate of coke formation for phosphorus containing naphtha.

CHAPTER 2

LITERATURE REVIEW

Although several workers have studied the coke formation during pyrolysis of pure hydrocarbons, very meagre information is available on rates of coke formation during naphtha pyrolysis.

Coke formation during methane pyrolysis was studied by Hirt and Palmer (1967) between 1163 and 1373 K and an activation energy of 432 MJ/kmole was reported. Johnson and Anderson (1972) studied the coke formation from acetylene at temperatures ranging from 773 to 1273 K and observed both coke and polymer as the products. They suggested that coke and polymer were formed by two competing parallel reactions in the gas phase. Albright and McConnell (1978) investigated the rate of coke formation in ethane pyrolysis and found that the coking phenomenon was significantly affected by the material of construction of the pyrolysis tube and also on the pretreatment given to the reactor. An activation energy of coke formation of 250 to 290 MJ/kmole was reported.

The pyrolytic behaviour of unsaturated hydrocarbons was investigated by Kinney and Del Bel (1954) and they postulated that coke was formed from a stepwise condensation of the aromatic rings. Virk et al. (1974) proposed that coke formation occurred from aromatic compounds, mainly from benzene. Shah et al. (1976) studied the coke formation during thermal cracking of n-octane between 1023 to 1073 K. The coking rate was high during the

initial stages of the reaction and then reduced to an asymptotic value. They also observed that the amount of coke formed increased with an increase in surface to volume ratio of the reactor. Further air (or oxygen) treatment activated the reactor surface to induce more coking whereas H_2S treatment passified it. The rates of coke formation during naphtha pyrolysis in an annular reactor were reported by Newsome and Leftin (1979). The coking rates were found to depend on the run time, inlet steam and hydrocarbon partial pressure and temperature. The specific rate of coking was independent of the surface to volume ratio of the reactor.

Sundaram and Froment (1979) designed a jet-stirred completely mixed reactor which allowed the kinetics of the main pyrolysis reaction and kinetics of coking to be determined simultaneously. The coke deposition was measured continuously by suspending a small cylinder of the same material as the reactor, into the reactor from an electrobalance. For propane pyrolysis, the coking rates were best represented by a model which assumed that coke was formed from propylene by a first order reaction, whereas the coke formation in ethane pyrolysis was modelled as a first order reaction from C_4^+ hydrocarbons (Sundaram et al. 1981). Trimm and Turner (1981a) also studied the coke formation in propane pyrolysis in a jet-stirred reactor and found that once the reactor surface was covered with carbon, the rate of coke deposition was independent of the nature of the surface at all temperatures. Pramanik and

Kunzru (1985) investigated the pyrolysis of n-hexane and kinetics of coking in a jet-stirred reactor in the temperature range of 993-1083 K. The experimental coking rates could be adequately fitted by a model in which ethylene was the coke forming species. Kumar and Kunzru (1985) also used a jet-stirred reactor to study the coke deposition during naphtha pyrolysis and the rate of coke formation was modelled by an approximately second order reaction involving the aromatics. Sahu (1986) investigated the effect of aromatic and sulphur content of the naphtha feed on the rate of coke formation.

It has been reported that the surface of reactor significantly affects the coke formation during hydrocarbon pyrolysis. Various investigators have shown that the metals present in the reactor surface activate the coke formation. The presence of metals in coke during ethylene cracking has been reported by Albright and co-workers (1978), who have demonstrated that such metals can catalyze the formation of additional coke. Research of Albright and co-workers (1979) on the pyrolysis of hydrocarbons over Inconel 800 surfaces showed iron to be the predominant metal in the coke.

Although coke formation during pyrolysis is undesirable, very few investigators have studied methods for inhibiting coke formation.

Since the reactor walls catalyze the coke formation, a common method for inhibition of coking during pyrolysis is to passivate the reactor walls. Reduction of coke formation

during the pyrolysis of ethane (Albright and McConnell, 1978), propane (Trimm and Turner, 1981b) and octane (Shah et al., 1976) on presulphiding the reactor wall has been reported. Bajus et al. (1981, 1983) reported the effect of thiophene, dibenzyl sulphide and dibenzyl disulphide on reaction kinetics and coking of steam cracking of heptane in stainless steel tubular reactors with relatively large surface areas. The metal sulphide, which passivated the reactor surface, inhibited the coke deposition considerably.

Brown et al. (1982) deposited a silica coating on preoxidized steel substrates by the decomposition of an alkoxysilane in a carrier gas. With such an inert coating, coke formation was reduced by a factor of 10 in short terms tests and by a factor ^a of ~~of~~ 3-4 in longer term tests during pyrolysis in the temperature range of 973 to 1073 K. Tomita et al. (1977) have developed a sintered catalyst comprising of calcium oxide, aluminium oxide and less than 0.2 wt per cent silicon dioxide. Considerable reduction in coke formation during naphtha pyrolysis was found with this catalyst. Showa (1983) reported that incorporating alkali metals and their oxides to Ni-Cr alloys or HK-40 was effective in significantly reducing the rate of coke formation during the cracking of steam-hydrocarbon mixtures. The reactor tubes of alloy steel were modified with lithium and casted whereas the HK-40 tubes were either micro alloyed with barium or flame-sprayed with a powder of HK-40 and lithium-oxide (LiO_2).

$[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2 \text{ Ph PS}(\text{OC}_2\text{H}_5)] - (\text{I})$ or $[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2 \text{ Ph PS}(\text{OC}_2\text{H}_5)] - (\text{II})$ were effective in controlling coke formation during pyrolysis of liquid hydrocarbons without affecting the product yields.

From the above literature survey, it is clear that not much information is available on inhibition of coke formation during naphtha pyrolysis. The effect of phosphorus compounds on the rate of coke formation during steam cracking of naphtha has not been well studied. In addition, no information is available on the effect of sodium silicate on the rate of coke formation.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1. Experimental Apparatus:

The experiments were conducted in a jet-stirred reactor. A schematic diagram of the equipment is shown in Figure 1. Liquid naphtha and water from separate graduated burettes were pumped by a double acting reciprocating pump which could be adjusted for flow rates in the range of 0.4 to 30.0 cc/min. Steam, which was used as an inert, was generated in a vaporizer (1.5 kW) and mixed with naphtha. The mixture of hydrocarbon and steam was passed through another preheater (1.5 kW) where the mixture was heated to approximately 770 K. The heated mixture was then led into the reactor which was just above the preheater. The product gases from the reactor exited through a central outlet tube which extended above the preheater and was constructed from 25 mm O.D. SS 316 tubing.

The preheater-reactor assembly was such that good mixing could be achieved in the reactor. It was made from a 25 mm I.D. SS 316 tubing and the reactor length and volume were 2.3 cm and 11.2 cm³, respectively. The wall separating the reactor and preheater contained thirty five one mm holes, distributed uniformly, which acted as nozzles and ensured good mixing inside the reactor. To provide uniform distribution of the inlet mixture into the reactor, the preheater was packed

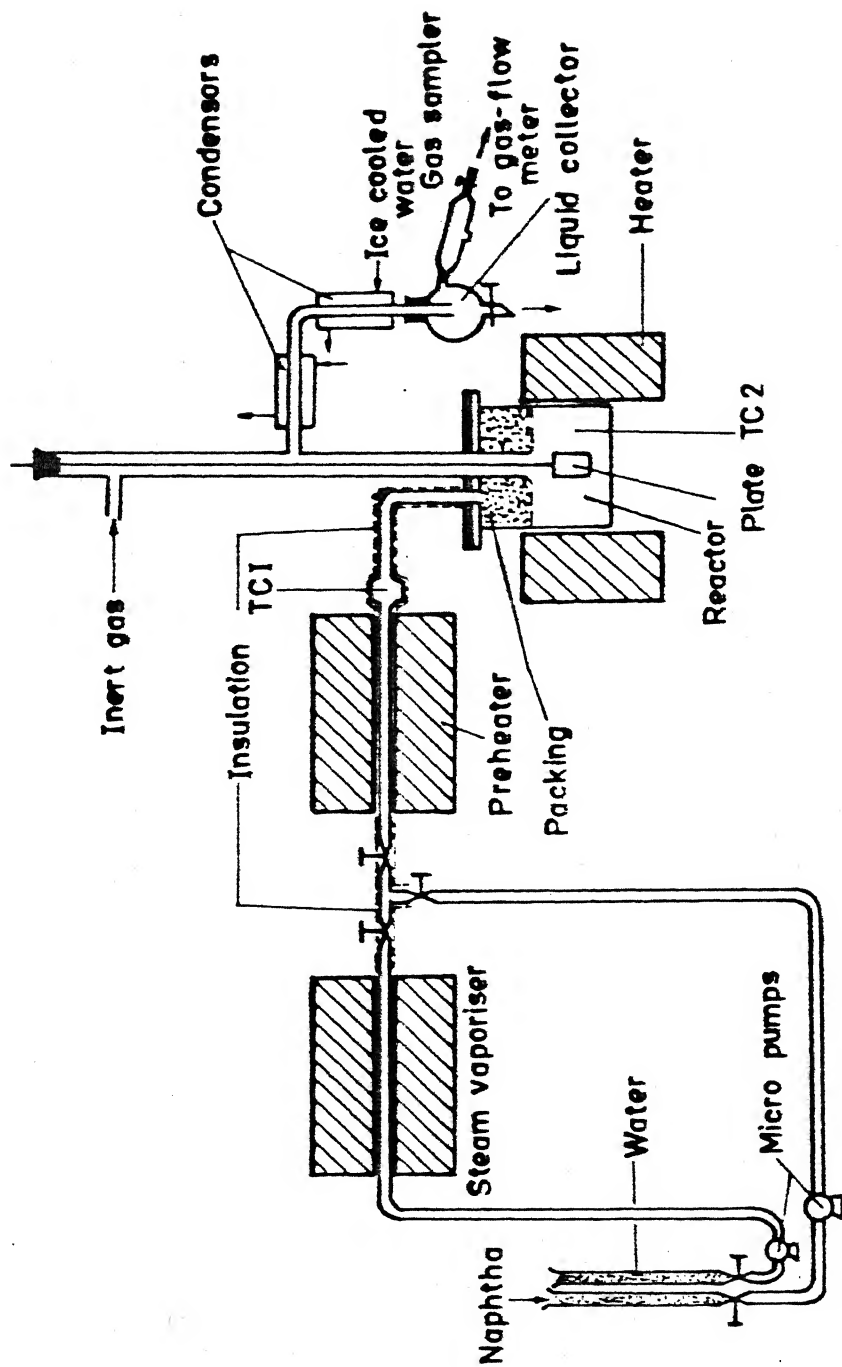


Fig.1 Schematic diagram of the experimental setup

with crushed ceramic beads. The preheater-reactor assembly was heated in a controlled electric furnace. The temperature of the reactor was measured and controlled by a temperature-indicator-controller (Model CT 806, Century Instrument) which was connected to a chromel-alumel thermocouple placed in a thermowell which extended into the centre of the reactor. The reactor temperature could be controlled to within $\pm 2^{\circ}\text{C}$ of the set value. There was a large temperature gradient in the preheater zone, but, in all the runs, the axial temperature gradient in the main reactor was negligible.

For the measurement of coke, a small rectangular plate of the same material as the reactor was suspended by means of a fine wire into the central portion of the reactor through the central outlet tube. The plate was weighed on an electro-balance and resuspended at the centre of the reactor. This was done at periodic intervals during the course of a run. To prevent reaction products from entering the outlet tube, a small flow of nitrogen was passed from the top through the side exit of the outlet tube. The reaction mixture was quenched by passing through two ice-water cooled condensers placed in series. The liquid product was collected and the non-condensables passed through a sampling valve and vented.

3.2 Experimental Procedure:

Experimental runs were initiated by first heating the reactor to a temperature 10-12 K higher than the desired temperature. After the temperature had stabilized, the reactor was flushed with steam for 45 minutes to ensure an inert

to the desired value and naphtha feed started. Since pyrolysis is endothermic, the reactor temperature dropped by 10-12 K once the reaction commenced. After the temperature had restabilized, at the new value, a small rectangular plate was suspended by means of a fine wire into the central portion of the reactor through the central outlet tube. The suspended plate was removed from the reactor at thirty minute intervals, weighed on an electrobalance and resuspended. The accuracy of the balance was 0.01 mg. To prevent any oxidation of the deposited coke, the plate was pulled up slowly through the outlet tube so that it cooled to 473-523 K in the relatively cooler portion of the outlet tube. A run was continued till the rate of coke formation become constant. The total duration of each run varied from 4-5 hours. At the completion of the run, the reactor was flushed with steam and the deposited coke on the plate and reactor burnt by passing heated air through the reactor for approximately 30-40 minutes. After decoking the plate was cleaned with emery paper. A similar procedure was followed for both coated and uncoated plates. In this study, due to the limitations of the experimental set-up, simultaneous measurement of the coke deposition and the reactor effluent was not possible. The reaction products together with the unreacted naphtha and steam were directly vented through the condensers.

For coating the plate with sodium ortho-silicate (m.p. 1291 K), an aqueous solution of sodium-ortho-silicate was prepared and the dried, cleaned and preweighed plate immersed

into this. The plate was removed from the solution after a few minutes and a thin impervious layer of the solution adhered on the plate. The plate was then heated slowly and uniformly at 473°K for 5 minutes to evaporate the water and then reweighed. If the weight of the sodium-ortho-silicate deposited was different from the desired value, the concentration of sodium-silicate in the aqueous solution was appropriately adjusted and the procedure repeated. A thin, uniform coating of sodium-ortho-silicate of the desired weight was thus obtained. The sulphur and phosphorus content of naphtha were varied by adding appropriate amounts of thiophene and triethyl phosphite to the naphtha feed.

CHAPTER 4

RESULTS AND DISCUSSION

To study the coke formation during naphtha pyrolysis, experiments were conducted at atmospheric pressure in the temperature range 1088 to 1108 K. Two types of naphtha feed were used in this study. In the initial stages of this work, the feed was a light naphtha (Naphtha I) obtained from Bharat Refineries, Bombay and the characteristics of this naphtha are given in Table 1. Additional quantities of this naphtha could not be obtained due to various problems and subsequent experiments were conducted with a naphtha (Naphtha II) obtained from Indian Explosive Limited, Kanpur. The characteristics of this naphtha are given in Table 2. The weight ratio of steam to naphtha, δ , was varied from 0.50 to 0.71 kg/kg. The phosphorus content of the feed was varied from 50 to 1000 ppm by adding triethyl phosphite $[(C_2H_5O)_3P]$ to the naphtha. The sulphur content of the feed was varied from 100 to 400 ppm by adding thiophene to the feed.

4.1 Effect of Sodium Silicate on Coke Formation:

To study the effect of sodium silicate, the concentration of sodium silicate on the metal plate was kept fixed at 5.20×10^{-3} kg/m². The runs were conducted at 1078 K,

TABLE 1: CHARACTERISTICS OF NAPHTHA (I) FEEDProperties:

(i)	Density (298 K)	0.701 gm/ml
(ii)	ASTM Distillation	°C
	IBP	47
	5%	59
	10%	63
	50%	87
	90%	119
	95%	129
	FBP	156
(iii)	PONA	wt.%
	Normal Paraffins	33.7
	Total Paraffins	73.6
	Naphthenes	17.4
	Benzene + Toluene + Xylene	8.5
(iv)	Total Sulphur	0.05
	Average molecular weight	91

TABLE 2: CHARACTERISTICS OF THE NAPHTHA (II) FEEDProperties:

(i)	Density (298 K)	0.711 gm/ml
(ii)	ASTM Distillation	°C
	IBP	89
	5%	97
	10%	102
	50%	123
	90%	149
	95%	158
	FBP	177
(iii)	Olefins	0.1 wt.%
	Aromatics	20 wt.%
(iv)	Total sulphur	5-10 ppm

1088 K and 1108 K keeping δ and space time constant at 0.71 kg/kg and 0.53 s, respectively. The effect of sodium silicate on coking rates both on uncoated and coated Inconel 600 surfaces is shown in Fig.2. As can be seen from this figure, coking rates were significantly reduced in the presence of sodium silicate. It was observed that the variation of coking rate with run time was different on coated and uncoated surfaces. For uncoated surfaces, the rate of coke formation was initially high and then decreased asymptotically to a constant value. Other workers have also reported a similar trend for the rates of coke formation during the pyrolysis of naphtha (Newsome and Leftin, 1979; Kumar and Kunzru, 1985; Sahu, 1986; Bahadur, Sahu and Kunzru, 1987). Initially, the metal surface is bare and devoid of any coke, so that the bare surface catalyzes the coke formation. With increasing run time, coke progressively covers the surface and metal catalytic activity is gradually reduced. The asymptotic coking rate, corresponds to coke deposition on a surface fully covered with coke. In case of sodium silicate coated surfaces, the coking rates were found to be very low initially, increased to a maxima in approximately 90-120 minutes and finally reduced to a constant value in approximately 180-210 minutes. A similar trend for the variation of coking rate with run time has been reported for K_2CO_3 coated surfaces during the pyrolysis of n-hexane (Mandal and Kunzru, 1986) and naphtha (Bahadur, Sahu and Kunzru, 1987). A possible reason for this trend could be

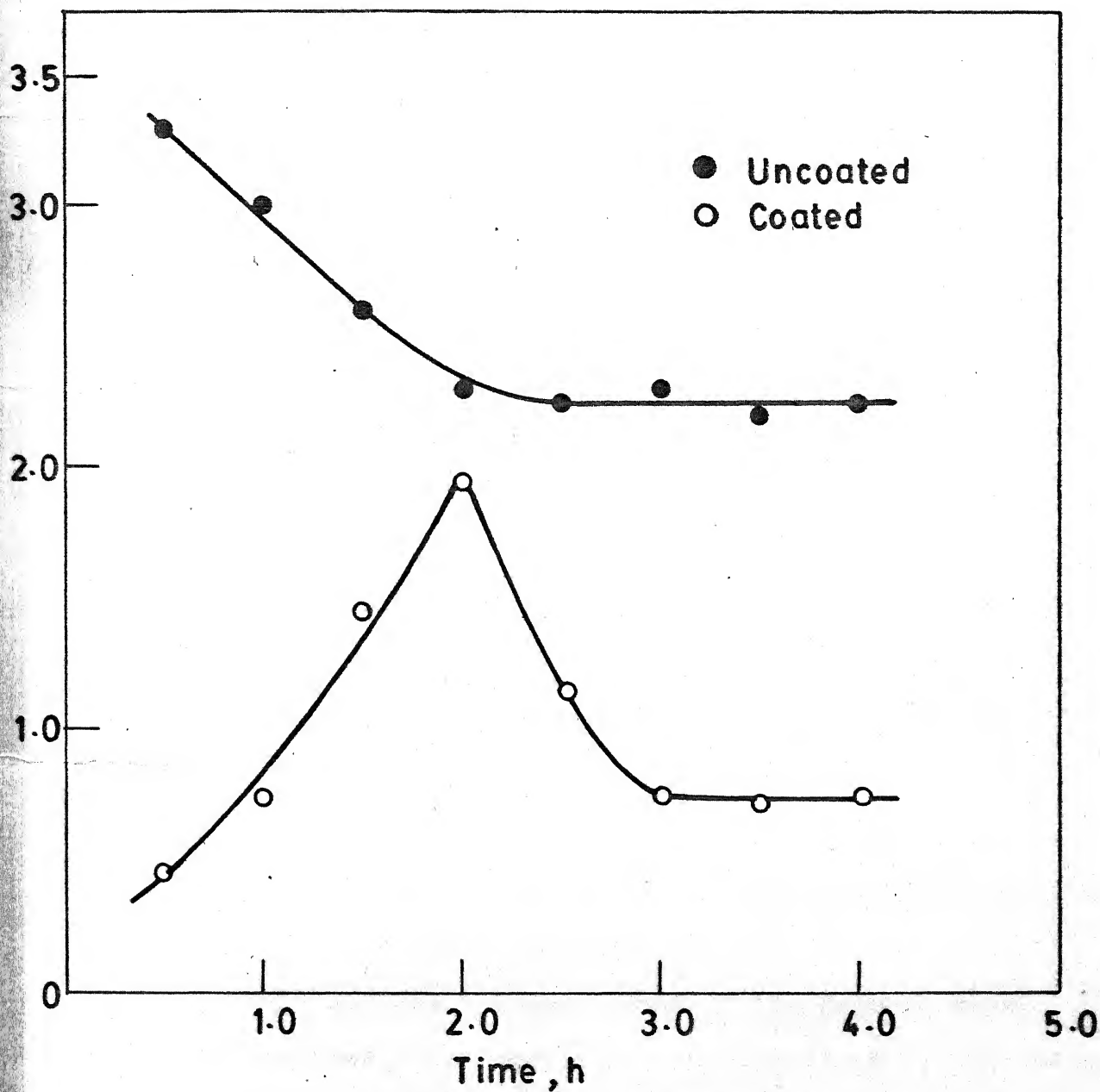


Fig. 2 Comparison of rate of coke formation on sodium silicate coated and uncoated Inconel 600 surfaces ($T = 1088\text{ K}$, $S = 0.71\text{ kg/kg}$, $\tau = 0.53\text{ S}$)

that the coke which is deposited initially catalyzes further coke formation due to the migration of some metal particles on the top of the growing carbon. As the amount of coke deposited increases, these metal particles start becoming encapsulated with coke and the metal catalytic activity starts to decline. This point would correspond to the maxima in the coking rate plot. The metal activity further reduces because of more coke deposition with time and ultimately all the metal particles are encapsulated, giving a constant coking rate.

The effect of temperature on the rate of coke formation was determined by varying the temperature in the range 1078-1108 K keeping δ , spacetime and concentration of sodium silicate fixed at 0.71 kg/kg, 0.53 s and 5.2×10^{-3} kg/m² respectively. The results are shown in Fig.3. As can be seen from this figure, the coking rates increased with increasing temperature. The trend is similar to the results which are reported during pyrolysis of n-hexane (Mandal and Kunzru, 1986) and naphtha (Bahadur, Sahu and Kunzru, 1987). The rate of coking increases with temperature because coke is formed from secondary reactions and once formed does not react further.

To study whether the reduction in the rate of coke deposition in presence of sodium silicate was due to the enhanced rate of the coke-steam reaction, runs were conducted at 1078 and 1108 K by replacing steam with nitrogen. δ and space time were kept fixed at 0.70 kg/kg and 0.53 s, respectively. The rate of coke formation on a sodium silicate coated plate in the presence

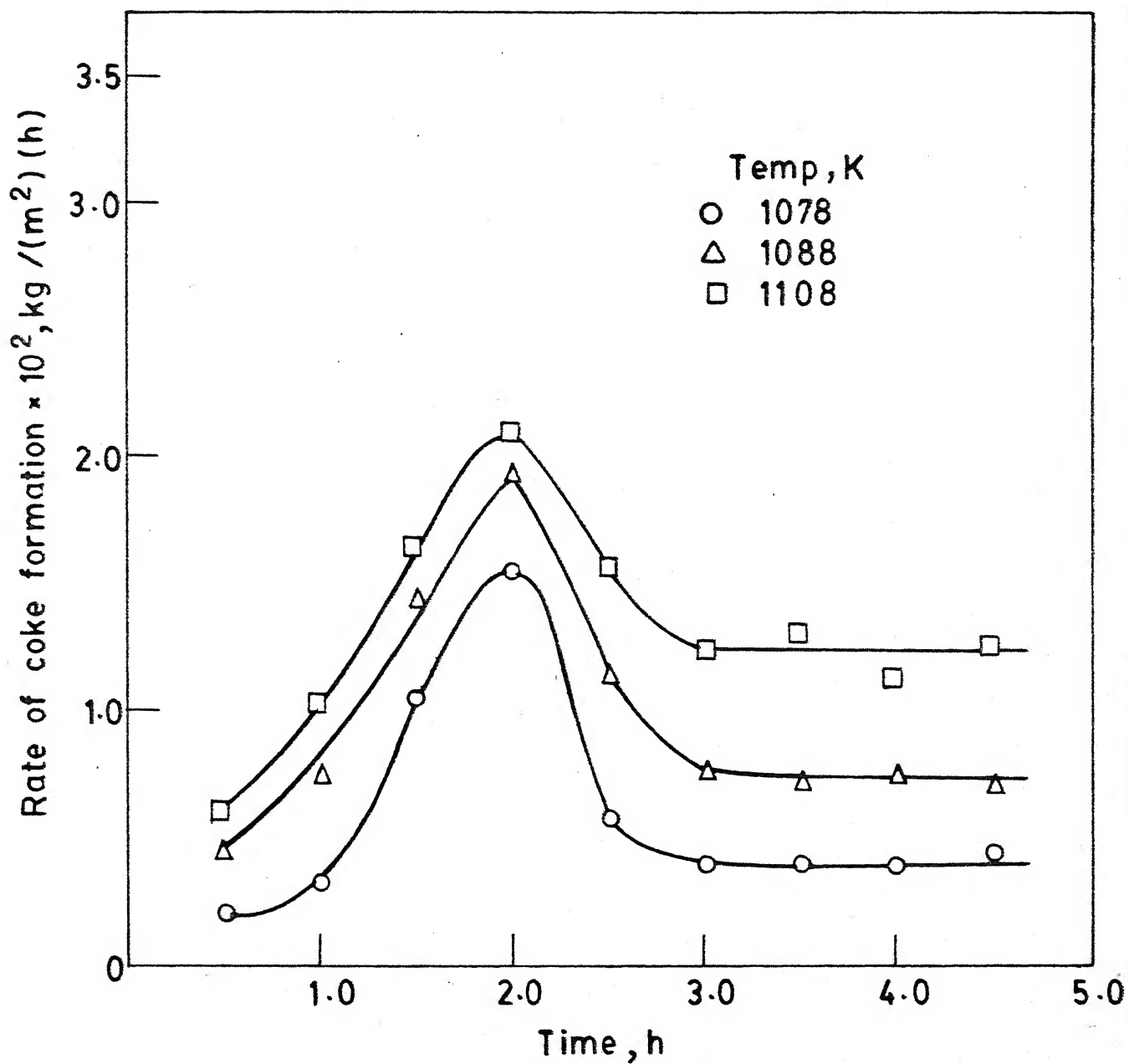
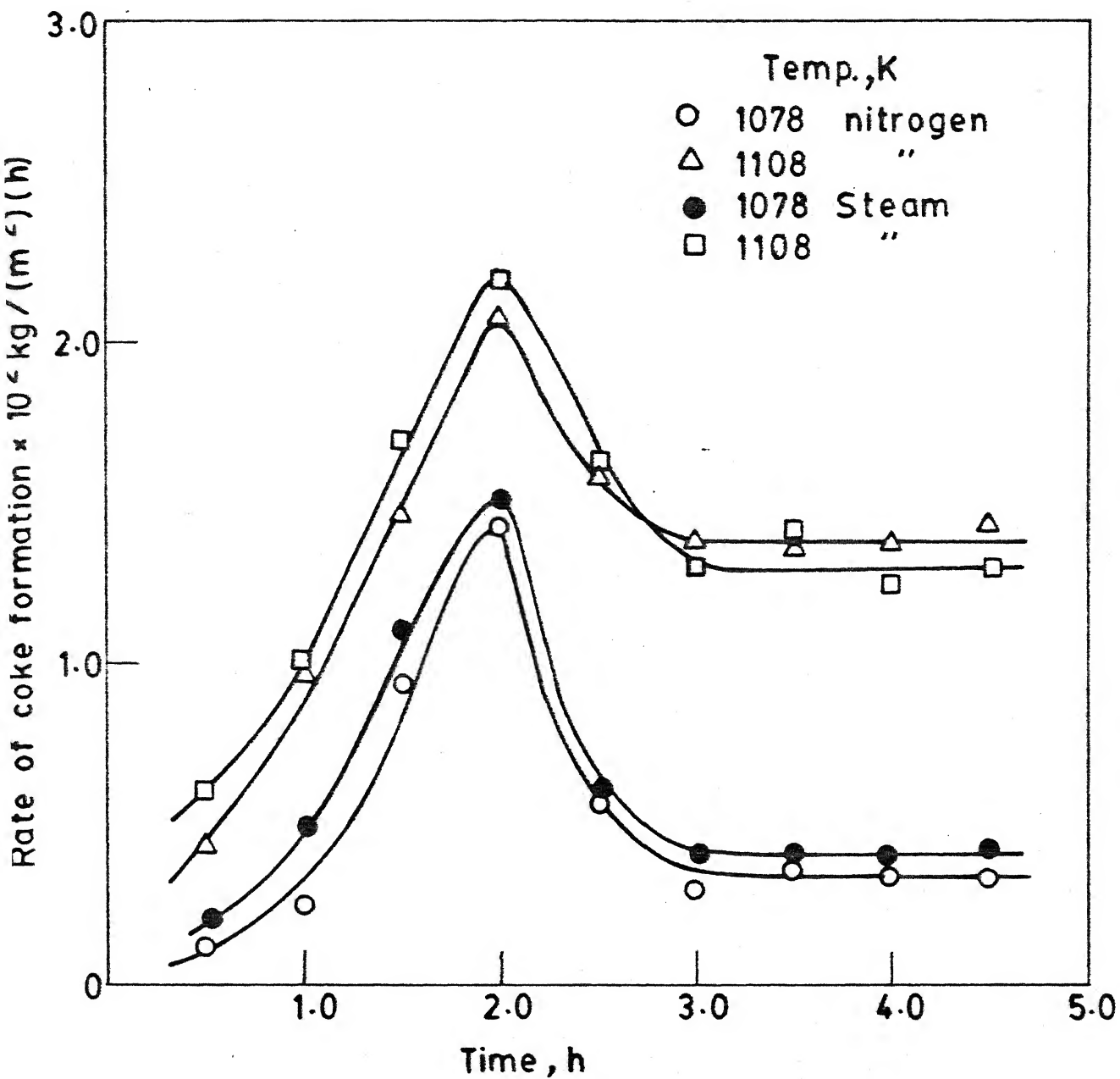


Fig. 3 Effect of temperature on the rate of coke formation on sodium silicate coated surfaces ($\delta = 0.71 \text{ kg} / \text{kg}$, $\tau = 0.53 \text{ S}$)

of nitrogen is shown in Fig.4. As shown in this figure, the rates of coke formation were identical irrespective of whether steam or nitrogen was used as the inert medium. This shows that the sodium silicate does not reduce the coking rate by catalytically gasifying the coke. Presumably, the reduction is due to the passivation of the metal surface. Contrary to these findings Mandal and Kunzru (1986) found that potassium carbonate did not reduce the rate of coke deposition in the absence of steam.

4.2 Effect of Decoking:

To investigate the effect of decoking on the rate of coke formation, the coking rates were first measured on a sodium silicate coated surface at 1088 K. The plate was then decoked by passing heated air for approximately 45 minutes. This decoked plate, without any further sodium silicate coating, was again suspended into the reactor and the run was continued till the constant rate was again attained. The same plate was decoked twice and each time coking rates with run time were measured. The results are shown in Fig.5. For runs on decoked surfaces, no maxima was observed in the coking rate. The coking rate decreased with time and finally approached an asymptotic value. The asymptotic coking rate increased as the number of decoking on the same plate were increased, which indicates that sodium silicate is being gradually lost from the surface during decoking. A similar trend has been reported during the pyrolysis of n-hexane (Mandal and Kunzru, 1986) and naphtha (Bahadur, 1986) on K_2CO_3 coated surfaces.



g. 4 Effect of diluent on the rate of coke formation on sodium silicate coated surface ($\delta=0.71 \text{ kg / kg}$, $\tau=0.53 \text{ S}$)

Since the rate of coke formation on a sodium silicate coated surface gradually increases with the number of decokings, it does not seem to be a suitable method for commercial coils. A continuous injection of a coke inhibitor would be a more effective method. With this constraint, a liquid inhibitor, soluble in either naphtha or water, was searched for and triethyl phosphite $[(C_2H_5O)_3 P]$, which is soluble in either naphtha or water, was selected as a possible inhibitor for reducing coke formation during naphtha pyrolysis. All the subsequent runs were conducted with Naphtha (II).

4.3 Effect of Phosphorus Content of Feed:

The effect of phosphorus content of the feed on the coke formation was studied by adding triethyl phosphite $[(C_2H_5O)_3 P]$ to the naphtha. The addition of various quantities of triethyl phosphite was so arranged that the phosphorus content of the feed varied from 50 to 1000 ppm.

The addition of triethyl phosphite reduced the rate of coke formation and the variation with run time for different phosphorus concentration in the feed at 1088 K is shown in Fig.6. It was observed that the rate of coke formation was initially high and then decreased asymptotically to a constant value in approximately 90-120 minutes. As can be seen from this figure, coking rates were significantly reduced in the presence of phosphorus. For instance, the presence of 100 ppm phosphorus in the feed reduced the rate of coke formation by 56%. It is comparable with the reduction of coke formation during pyrolysis in ethylene furnace (Boone, 1983). It has

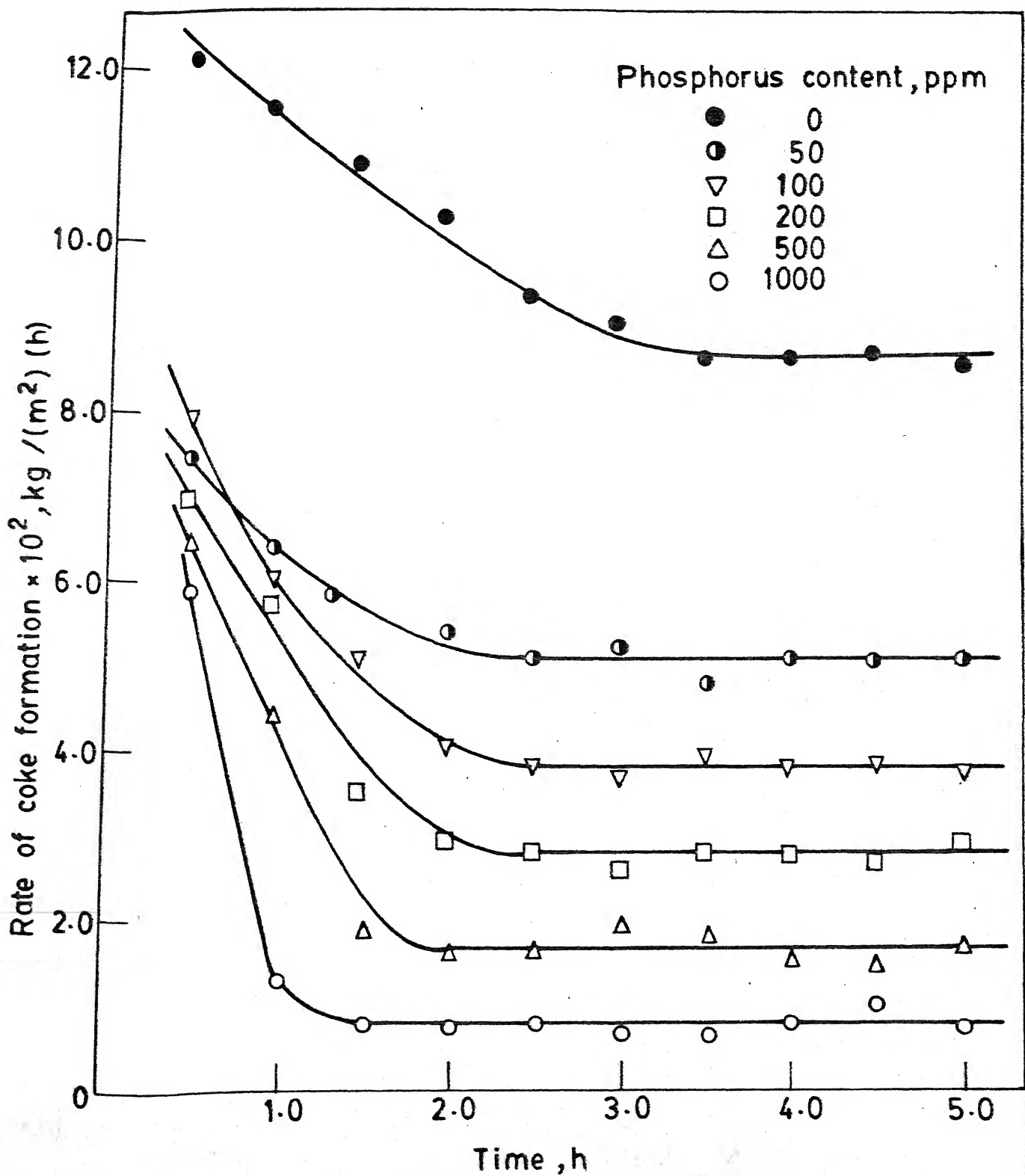


Fig. 6 Effect of phosphorus content on rate of coke formation
 ($T = 1088\text{K}$, $\delta = 0.70\text{ kg/kg}$, $\tau = 0.53\text{S}$, Sulphur in feed =

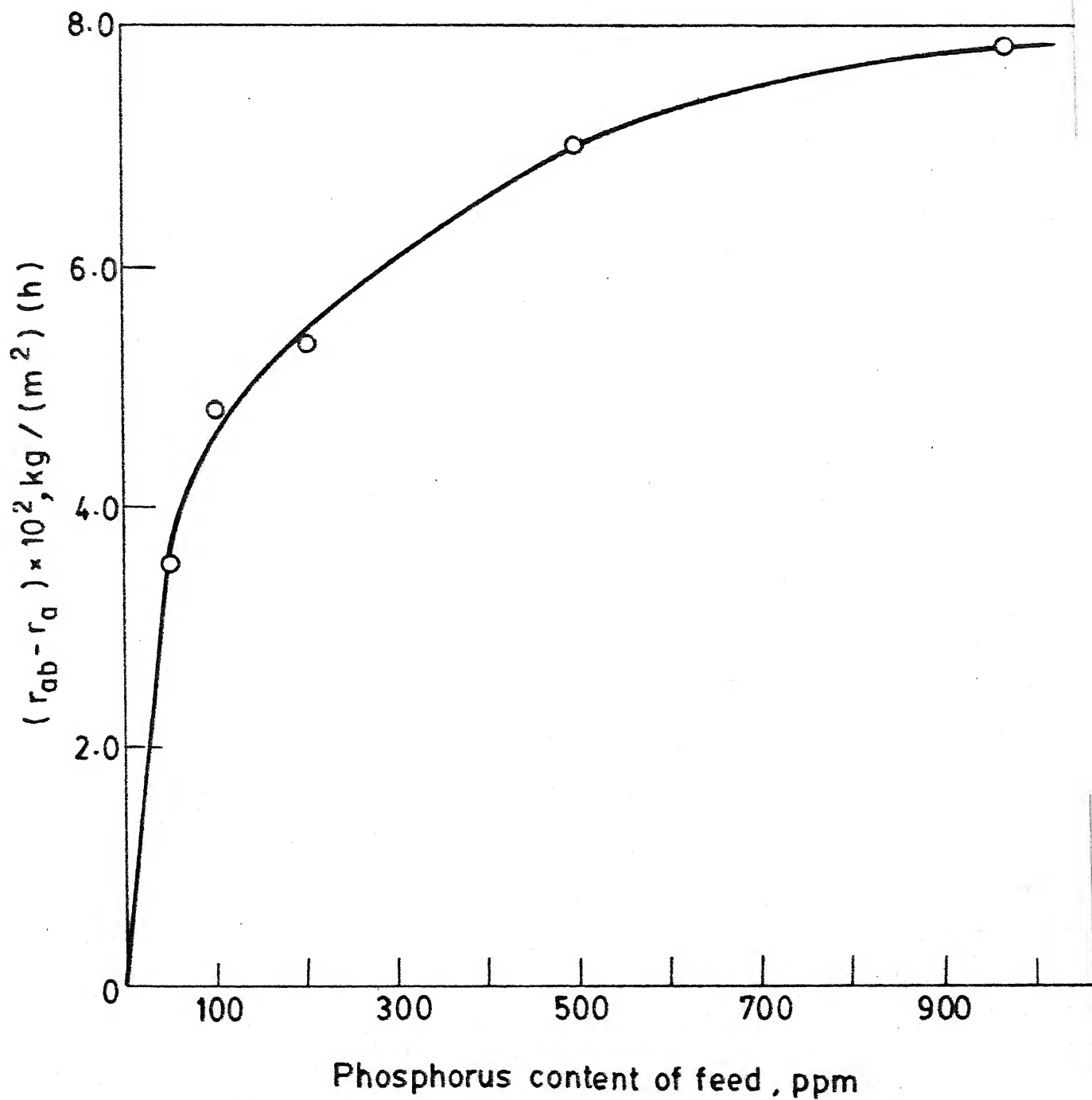


Fig. 7 Reduction in asymptotic rate of coke formation with phosphorus content ($T = 1088 \text{ K}$, $\delta = 0.70 \text{ kg} / \text{kg}$, $\tau = 0.53 \text{ S}$)

addition of 200 ppm phosphorus with the feed at 1088 K. The asymptotic rate of coke formation reduced with an increase in the phosphorus content of the feed but at higher phosphorus concentration the inhibition in coking rate was less. The decrease in the asymptotic rate of coke formation with increasing phosphorus content of the feed is shown in Fig. As can be seen from this figure, the reduction in the rate of coke formation was initially higher and then gradually decreased such that at high concentration of phosphorus, the coking rate approached a constant value.

To check whether or not the addition of phosphorus had an effect on the primary pyrolysis reaction, the total gas and liquid yields for different phosphorus concentrations were measured and these are shown in Table 3. It was observed that the total gas and liquid yields were approximately the same for different phosphorus concentrations. Although a detailed analysis of the liquid and gaseous products was not conducted the data on the total yields indicate that phosphorus did not have any effect on the primary pyrolysis reactions.

To investigate whether the reduction in the rate of coke formation in the presence of phosphorus was due to the enhanced rate of coke steam reaction, runs were conducted by replacing steam with nitrogen for identical temperature, δ and space time. As shown in Fig.8, the rates of coke formation were the same irrespective of whether steam or nitrogen was used as the inert medium. It was also noted that the total gas and liquid product yields were same with nitrogen or steam as the inert. The rates of coke formation were reproducible

TABLE 3: TOTAL GAS AND LIQUID YIELDS DURING NAPHTHA
PYROLYSIS

Temperature = 1088 K, $\phi = 0.7$ kg/kg, $\tau = 0.53$ s

<u>Run No.</u>	<u>Phosphorus, ppm</u>	<u>Sulphur, ppm</u>	<u>Liquid, cc</u>	<u>Gas, lit.</u>
1	0	0	18.5	40.6
2	100	0	20.0	40.0
3	200	0	20.0	39.0
4	500	0	20.5	40.2
5	1000	0	19.8	39.6
6	50	100	14.5	44.0
7	100	100	14.7	43.0
8	200	100	15.0	44.3
9	0	100	15.0	43.5

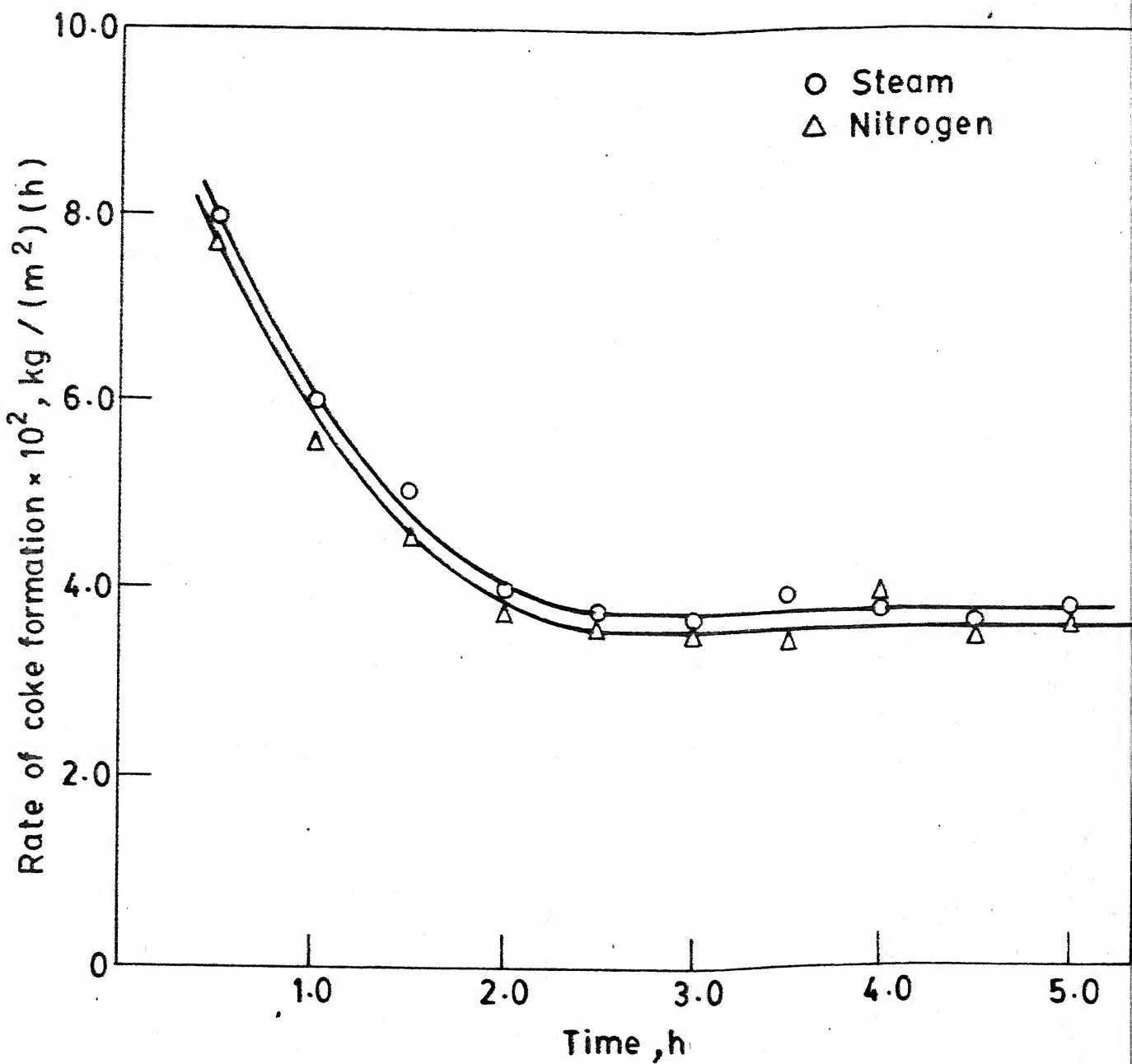


Fig. 8 Comparison rate of coking using Steam and Nitrogen as diluent ($T = 1088\text{K}$, $\delta = 0.70\text{kg/kg}$, $\tau = 0.53\text{S}$, $P = 100\text{ppm}$, $S = 0$)

to within $\pm 2\%$ and the total gas and liquid yields to within $\pm 4\%$.

The results of the above runs show that neither does the phosphorus take part in the homogeneous reactions nor does it catalyze the coke-steam reaction. Most probably, the phosphorus containing additive passivates the metal surface. Initially, the metal surface is devoid of any coke so that the bare surface catalyzes the coke formation. With increasing run time, a film of phosphorus-metal complex covers the surface and the metal activity is gradually reduced. The asymptotic coking rate would then correspond to the time when the concentration of the metal-phosphorus complex is in equilibrium with the concentration of phosphorus in the gas phase. This equilibrium concentration would depend on the reaction temperature and the concentration of phosphorus in the gas phase. Boone (1983) studied the effect of phosphorus containing chemical additive on the rate of coking for ethylene furnaces during pyrolysis and reported that phosphorus containing compounds significantly reduced the asymptotic coking rate. Moreover, when a pilot plant was examined after a treated run, a greenish-gray film was seen that had not been there on untreated runs. It has been reported (Naberezhnova et al., 1982) that the organo phosphorus compounds $[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{PhPS}(\text{OC}_2\text{H}_5)]$ (I) or $[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{PhPS}(\text{OC}_4\text{H}_9)]$ (II), were effective in controlling coking during pyrolysis of liquid hydrocarbons and the addition of (I) and/or (II) did not change the product yields.

To further check the hypothesis that the metal-phosphorus complex was in equilibrium with the concentration of phosphorus

in the gas phase, a run was made in which the feed was switched from phosphorus containing naphtha to phosphorus free naphtha after the asymptotic coking rate had been attained. The rates of coke formation were investigated by adding 100 ppm phosphorus as triethyl phosphite to the naphtha feed at 1088 K keeping δ and τ fixed at 0.70 kg/kg and 0.53 s, respectively. When the asymptotic coking rate had been attained, the phosphorus containing naphtha feed was switched off and naphtha without any added triethyl phosphite was passed. The results are shown in Fig.9. For phosphorus containing naphtha feed the coking rates were reproducible to within $\pm 1\%$ of those reported in Fig.6. When phosphorus-free naphtha was introduced, the rate of coking gradually increased and approached a constant value after 120-180 minutes of introducing the phosphorus-free naphtha. However, this asymptotic coking rate was lower than that measured when a fresh Inconel-600 surface was used. The results show that phosphorus affects the coking rate even after the additive supply has been terminated. This observation is in very good agreement with the results reported by Boone (1983) who found that an untreated run immediately following a treated run had a slightly lower than normal coking rate, due to a "memory" effect. Therefore, to maintain a reduced coking rate, continuous injection of the additive is necessary.

4.4 Effect of Process Variables:

Rates of coke formation varied with reactor temperature and inlet naphtha partial pressure. The effect of temperature

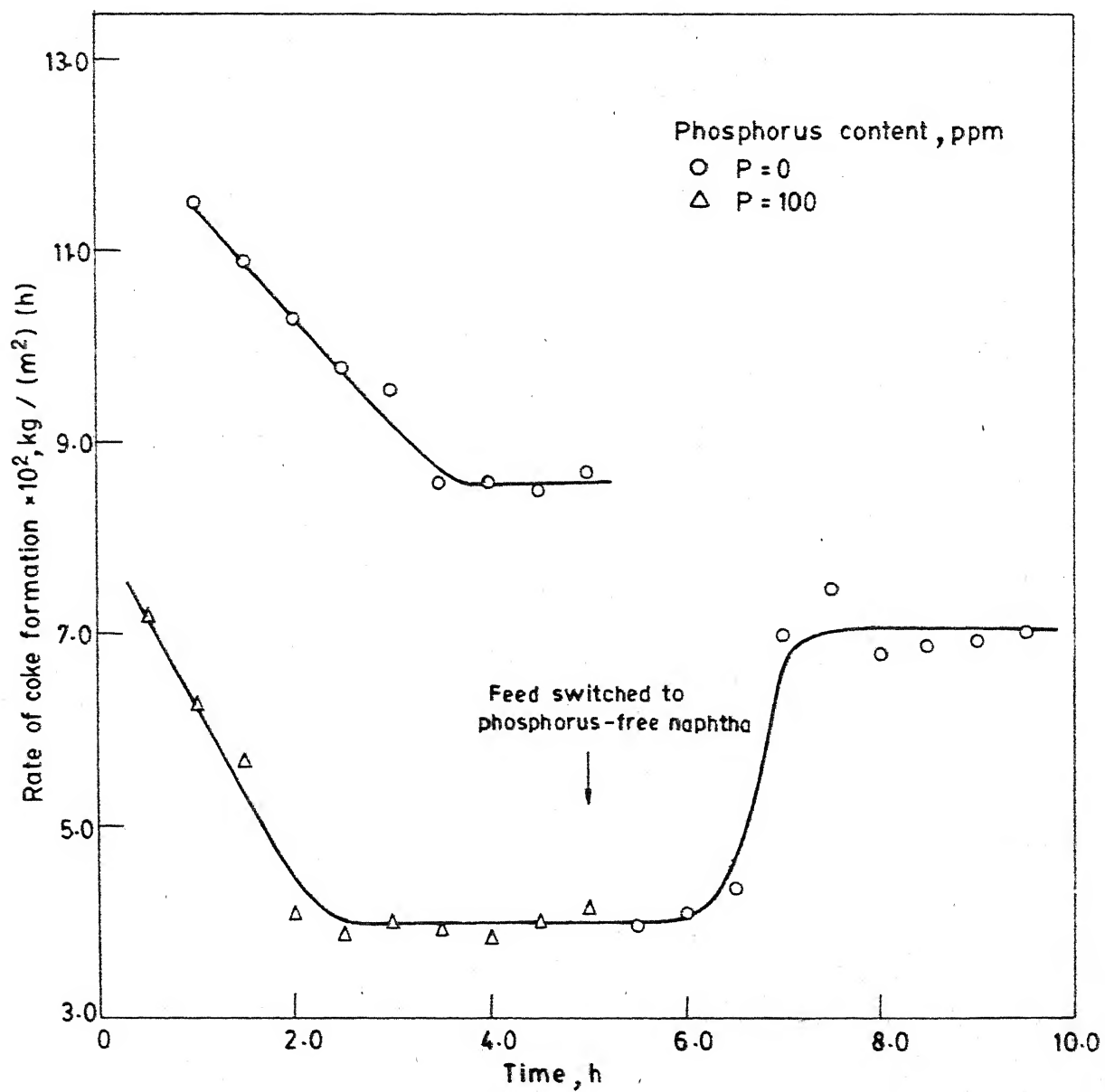


Fig. 9 Rate of coke formation when feed switched from phosphorus containing naphtha to phosphorus-free naphtha

was studied by varying the temperature in the range of 1088 to 1108 K, keeping δ and spacetime fixed at 0.70 kg/kg and 0.53 s, respectively. Since the variation of coking rates with run time was similar to that shown in Fig.6, the variation of only asymptotic coking rate with temperature and weight fraction of phosphorus is shown in Fig.10. As can be seen from this figure, coking rates increased with increasing temperature and decreased with increasing weight fraction of phosphorus. The trend for phosphorus-free naphtha is similar to that reported by other investigators (Kumar and Kunzru, 1985; Bahadur, 1986; Sahu, 1986). At phosphorus concentration of 200 ppm in the feed, increasing the reactor temperature from 1088 K to 1098 K, increased the rate of coke formation by 31.0 % whereas on increasing the temperature from 1088 K to 1108 K, the coking rate increased by 71.0 %. These results are in good agreement with the results for coke formation during pyrolysis of n-hexane containing 200 ppm of phosphorus (Boone, 1983). It was reported that on increasing the temperature from 1088 K to 1098 K, the rate of coking increased by 38% whereas from 1088 K to 1108K, the rate of coke formation increased by 66%. Increasing the temperature not only affects the rate constant for the coking reaction but also changes the equilibrium constant of the metal-phosphorus complex. This is discussed later (see section 4.7).

The effect of inlet partial pressure of naphtha on the rate of coking at a constant temperature of 1088 K both for

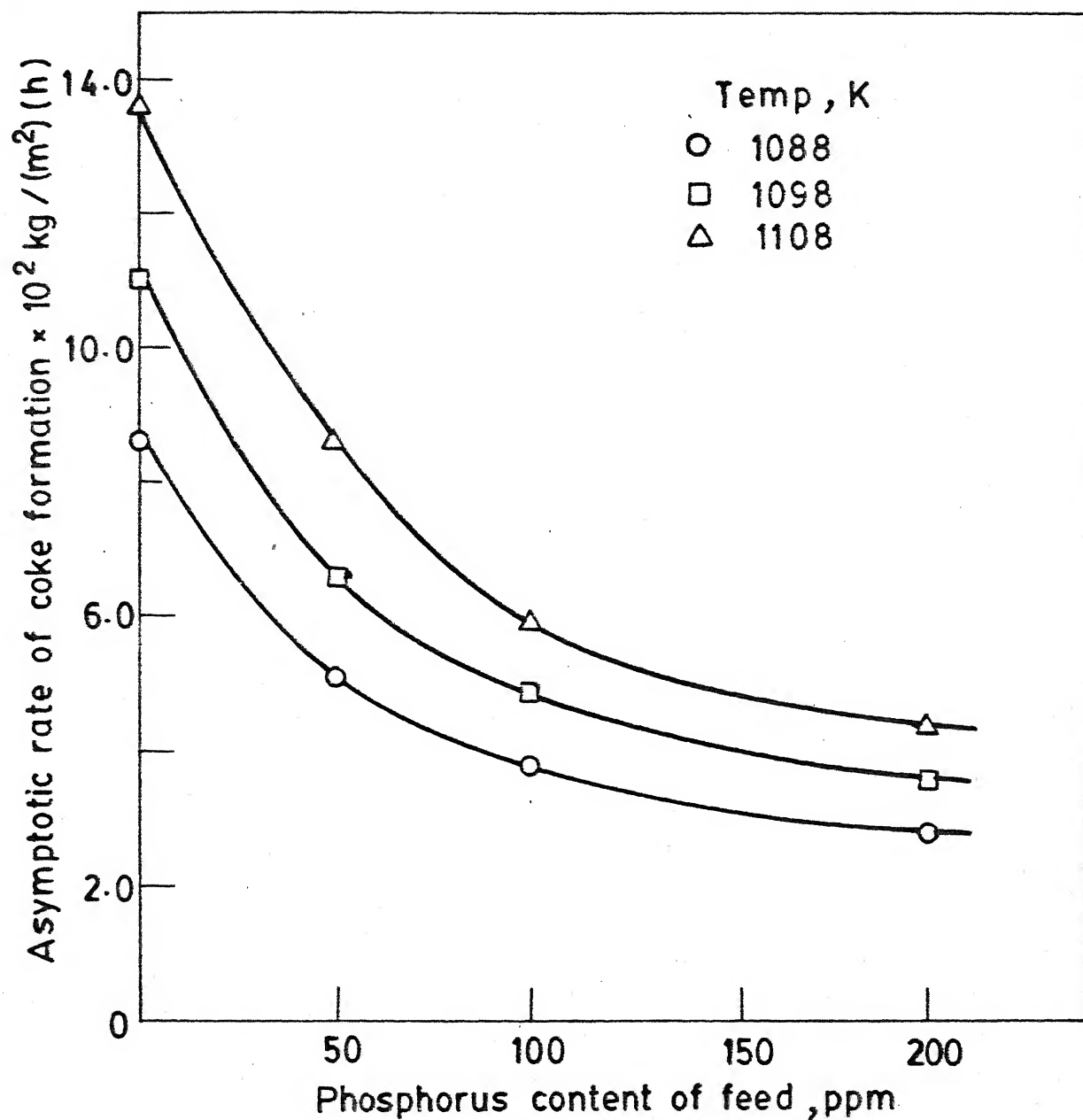


Fig. 10 Effect of temperature on asymptotic rate of coke formation for phosphorus containing naphtha
($\delta = 0.70$ kg / kg , $\tau = 0.53$ S)

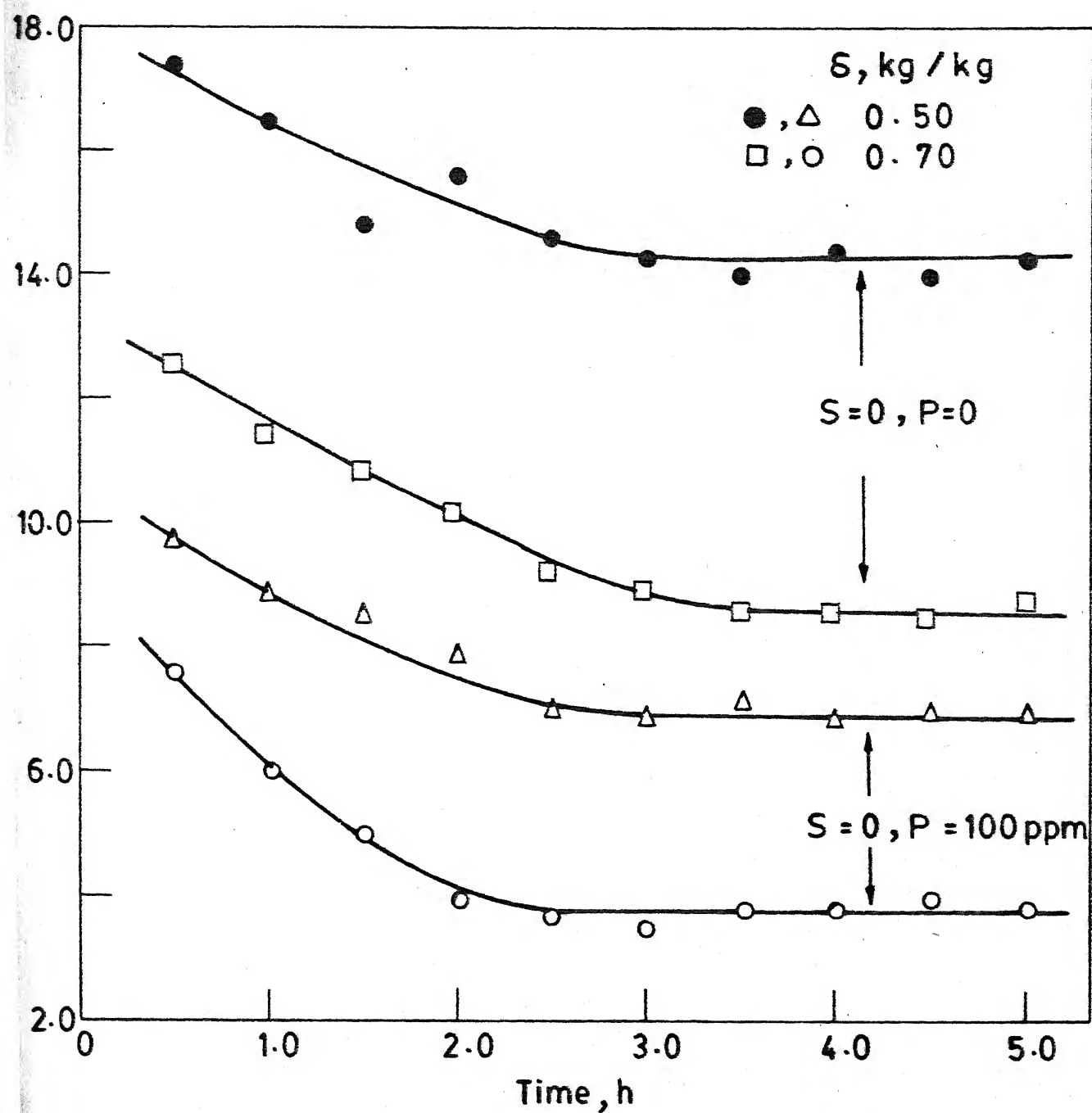


Fig. 11 Effect of inlet partial pressure of naphtha on rate of coke formation ($T = 1088\text{K}$, $\tau = 0.53\text{S}$)

phosphorus containing and phosphorus-free feed are shown in Fig.11. For both phosphorus containing and phosphorus-free feed, with increasing partial pressure of naphtha, the concentration of coke forming species is increased, thus increasing the rate of coke formation. At these temperature, the coke-steam reaction is not expected to be significant (Biba et al., 1978) and would not contribute to the reduction in rate of coking with increasing partial pressure of steam. As can be seen from this figure with decreasing partial pressure of naphtha, the reduction of coking rate is more significant for phosphorus-containing feed. For phosphorus containing feed, on increasing δ from 0.50 to 0.70 kg/kg, the rate of coke formation reduced by 43% whereas for phosphorus-free feed, reduction was 39%.

4.5 Effect of Phosphorus in Presence of Sulphur:

Sulphur compounds are well known to be effective in reducing coking during pyrolysis of hydrocarbons (Bajus et al., 1981, 1983). Most furnace feed stocks contain sulphur either added or naturally occurring and these help to control coking. Very limited data are available on the effect of phosphorus in the presence of sulphur compounds (Boone, 1983).

To investigate the effect of sulphur in phosphorus containing naphtha, thiophene was added to the feed. All the runs were conducted at 1088 K, with δ and τ kept fixed at 0.70 kg/kg and 0.53 s, respectively. To compare the effects of sulphur and phosphorus addition on the coking rate, runs were made in which either 100 ppm of sulphur and/or phosphorus was

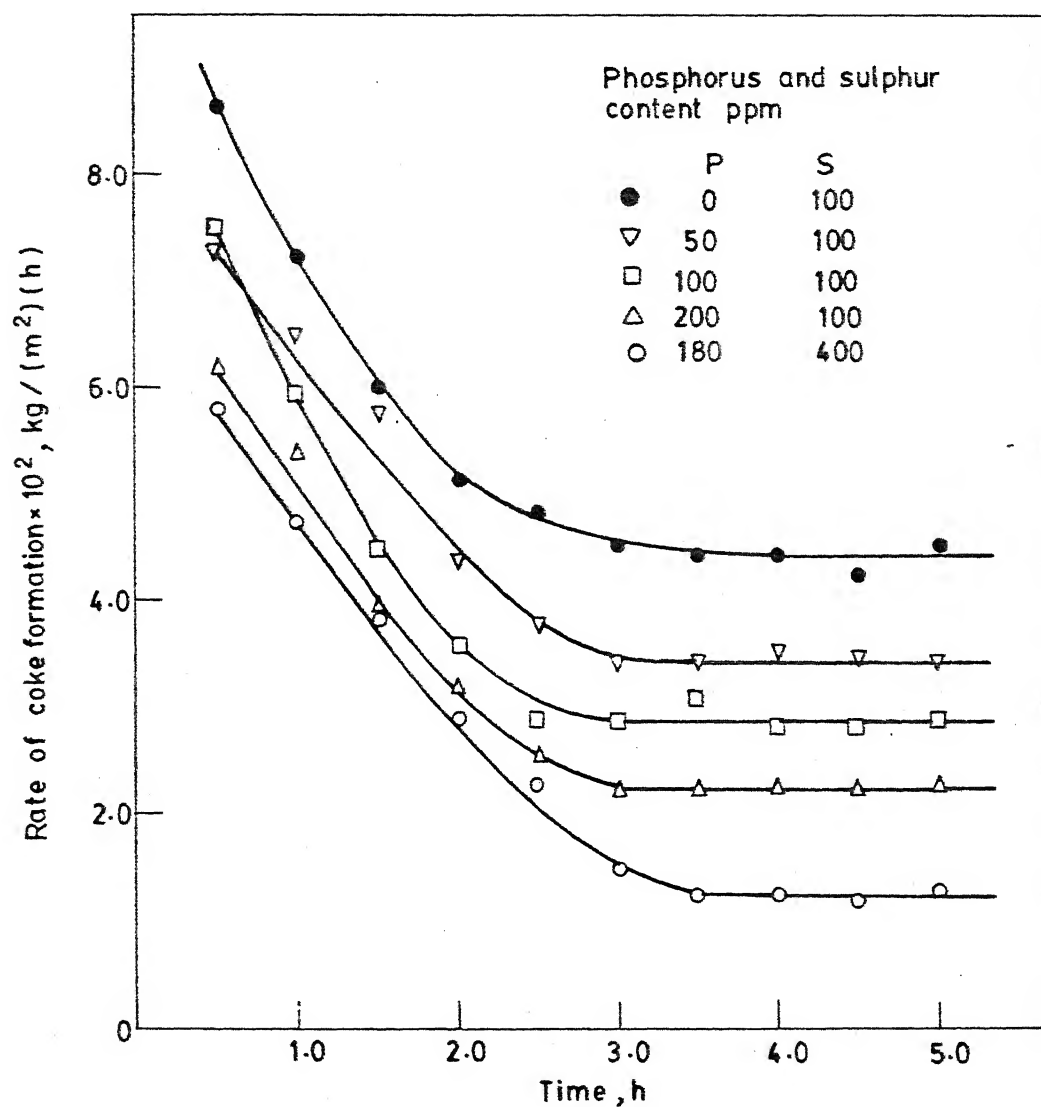


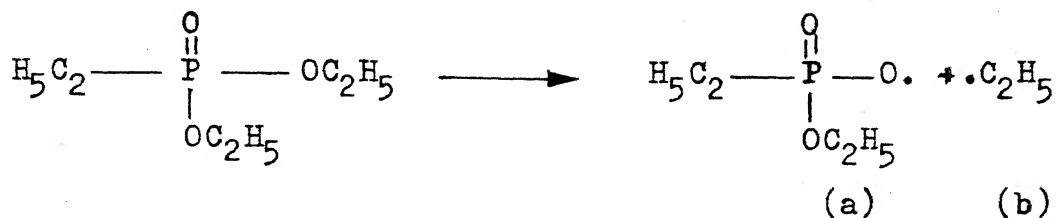
Fig. 12 Effect of phosphorus in presence of sulphur on the rate of coke formation ($T=1088K$, $\delta=0.70$ kg / kg, $\tau=0.53S$)

be seen from the figure, used in same concentration, phosphorus reduces the rate of coking more than sulphur. Moreover, with sulphur present in the feed, the percentage reduction in the coking rate is less than for sulphur free feed. The asymptotic coking rates were reduced with increasing phosphorus concentrations but not as much as when the feed contained no thiophene. For instance, for thiophene free naphtha, on increasing the phosphorus concentration from 50 to 100 ppm, the rate of coke formation was reduced by approximately 26% whereas the reduction in the coking rate was only 10% when both sulphur and phosphorus were present in the feed.

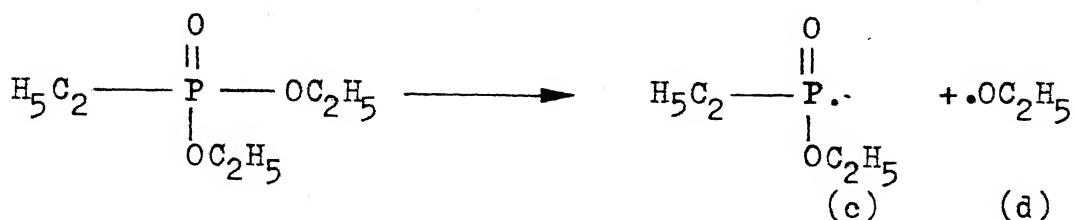
For a fixed sulphur concentration in the feed, the total gas and liquid yields did not change with varying phosphorus content of the feed. However, when the concentration of sulphur was varied, the gas and liquid yields also varied as shown in Table 3. For a fixed phosphorus concentration, with increasing sulphur concentration, the gaseous products were increased where as the liquid yields were decreased. Glass and Reid (1929) reported that when thiophene is present in the reaction mixture during pyrolysis, the aromatics can react with S. and .SH free radicals produced due to thiophene decomposition. It has been reported that addition of sulphur compounds reduced the rate of coking as well as yields of organic liquid products during pyrolysis of n-heptane (Bajus, et al., 1981, 1983) and naphtha (Sahu, 1986). Thus we can conclude that sulphur affects both the surface as well as homogeneous reactions where as phosphorus affects the surface reaction only.

A possible mechanism for the effect of phosphorus on the rate of coke formation is given below.

At high temperature (1078-1108 K) triethyl phosphite may break down in two ways:



or



The bond strength of O—C (1079.4 MJ/K mole) is more than that of O—P bond (598.9 MJ/K mole). Therefore, the cleavage of O—P

bond is more probable. The radicals $\text{H}_5\text{C}_2-\overset{\overset{\text{O}}{\parallel}}{\text{P}}-\text{O}\cdot$ and $\text{H}_5\text{C}_2-\overset{\overset{\text{O}}{\parallel}}{\text{P}}\cdot$

thus formed can react with the metal (M) to give $\text{H}_5\text{C}_2-\overset{\overset{\text{O}}{\parallel}}{\text{P}}-\text{OM}$ and $\text{H}_5\text{C}_2-\overset{\overset{\text{O}}{\parallel}}{\text{P}}-\text{M}$. The radicals $\cdot\text{OC}_2\text{H}_5$ and $\cdot\text{C}_2\text{H}_5$ either dimerize

or form compounds with the metal. The radicals $\text{H}_5\text{C}_2-\overset{\overset{\text{O}}{\parallel}}{\text{P}}-\text{O}\cdot$ and $\text{H}_5\text{C}_2-\overset{\overset{\text{O}}{\parallel}}{\text{P}}\cdot$ contain oxygen atoms which can supply electrons

and form a weak bond with the metal.

When metal atoms bond with the oxygen atoms, the migration of metal

atoms from the metal surface to the coke surface is inhibited. Metal atoms are known to migrate on top of the growing carbon and increase the coking rate (Albright & coworkers, 19). Moreover, due to steric hinderance of (a) and/or (c) radicals, migration of metal atoms is further inhibited. Thus triethyl phosphite reduces the coke formation. It has been reported (Naberezhnova et al., 1982) that in reducing coke deposition $[(CH_3COCH_2C(CH_3)_2 Ph PS(OC_2H_5))] or $[(CH_3COCH_2C(CH_3)_2 Ph PS(OC_4H_9)]$ is more effective than $[(PhO)_3P]$, which is perhaps due to steric hinderance. In case of thiophene, S. and .SH react with the metal forming metal sulphides, which reduces the coke deposition. Since thiophene does not have any oxygen atom nor does it offer a significant steric hinderance, the coke deposition is relatively more than with triethyl phosphite.$

4.6 Effect of Phosphorus in Presence of Potassium Carbonate:

The effect of potassium carbonate on reducing the rate of coke formation during naphtha pyrolysis of n-hexane (Mandal and Kunzru, 1985) and naphtha (Bahadur 1986) is well documented. To study the possibility of further reducing the rate of coke formation, a run was conducted at 1088 K in which naphtha containing 100 ppm phosphorus additive was passed over a Inconel 600 surface coated with $14.2 \times 10^{-3} \text{ kg/m}^2$ of K_2CO_3 . The results shown in Fig. 13 indicate that phosphorus had a negligible effect in reducing the rate of coking on a K_2CO_3 coated Inconel 600 surfaces. Although, there was some

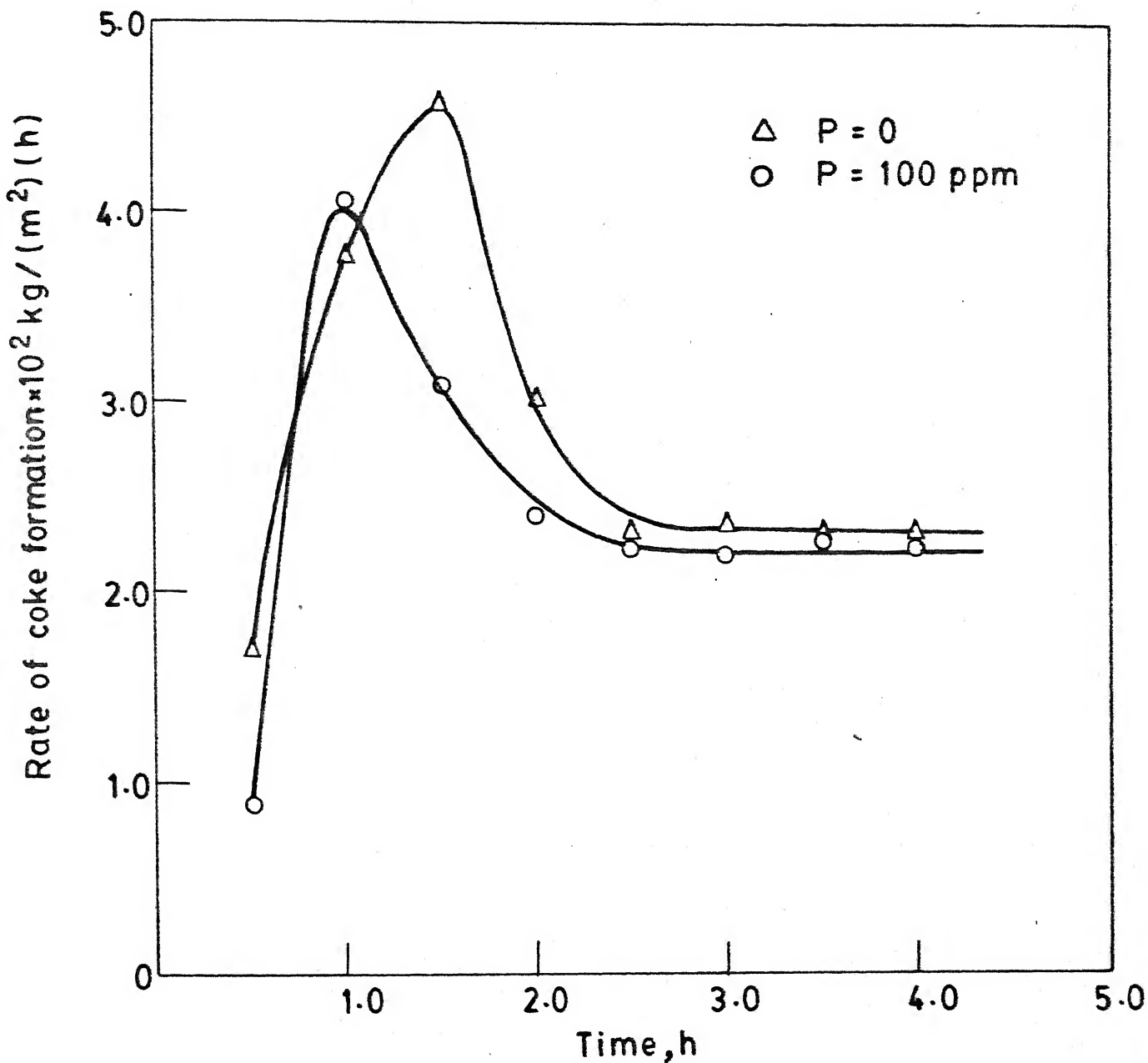


Fig. 13 Effect of phosphorus on the rate of coke formation on K_2CO_3 coated surface ($T = 1088 \text{ K}$, $\delta = 0.70 \text{ kg/kg}$, $\tau = 0.53 \text{ S}$)

difference in the initial stages of the experiment, the asymptotic coking rates were the same to within $\pm 2\%$. A plausible reason could be that either no metal-phosphorus complex is formed on a K_2CO_3 coated surface or the rate of coke formation on the complex is the same as that on a K_2CO_3 coated surface.

4.7 Modelling of Coke Formation During Pyrolysis of Phosphorus Containing Naphtha (Without Sulphur):

Coke formation during naphtha pyrolysis is a complex phenomena due to the various possible coke forming free radical reactions and the exact mechanism is still not clear.

Kumar and Kunzru (1985) postulated simple models involving either the reactant and/or products to model coke formation during naphtha pyrolysis and the asymptotic coking rate could be represented by the following expression

$$r_a = 1.68 \times 10^{23} \exp\left(-\frac{208600}{RT}\right) C_A^{1.98} \quad (1)$$

where r_a is the asymptotic coking rate in $(\text{kg coke})/(\text{m}^2)(\text{h})$ and C_A is the concentration of the aromatics in the reactor in $(\text{kg mole})/\text{m}^3$. Similarly, Sahu (1986) could model his data on coke formation during pyrolysis of naphtha by

$$r_a = k C_A^n \quad (2)$$

where the value of n was 1.32.

The exact mechanism for the reduction of coke formation due to addition of phosphorus is still not clear, and a simple

model has been proposed to explain the observed asymptotic coking rates.

Since phosphorus forms a complex with the metal, therefore at any time, coke formation occurs simultaneously on two types of surfaces viz. (i) surface covered with metal-phosphorus complex and (ii) metal surface which has not taken part in the complex formation. The asymptotic coking rate corresponds to the time when an equilibrium concentration of the complex has formed on the surface. This equilibrium concentration would depend on the partial pressure of phosphorus in the gasphase and the reaction temperature. From the available data, it seems that phosphorus does not affect the gas phase reactions leading to the formation of the coke precursors and only reduces the rate of the surface reaction.

Thus, assuming that coke is only formed from aromatics, the asymptotic coking rate, r_a , can be expressed

$$r_a = k_p y_P C_A^n + k_m (1-y_P) C_A^n \quad (3)$$

where r_a is the asymptotic coking rate,

y_P is the fraction of the metal surface covered with metal-phosphorus complex,

k_p is the rate constant for coke formation on a surface completely covered with phosphorus complex,

k_m is the rate constant for coke formation for a phosphorus free naphtha feed and

C_A is the aromatic concentration in the reactor. It should be noted that k_m , k_p and y_P depend on temperature.

Assuming that the rate at which the metal complex is formed is proportional to the product of the phosphorus

concentration in the gas phase and the fraction of surface area occupied by the complex, we obtain

$$\left(\frac{dy_P}{dt}\right) = k_f P(1-y_P) - k_r y_P \quad (4)$$

and at equilibrium $\left(\frac{dy_P}{dt}\right) = 0$.

$$\text{or} \quad y_P = \frac{K_P P}{1 + K_P P} \quad (5)$$

where K_P , equal to (k_f/k_r) , is the equilibrium constant for the complex formation and P is the weight fraction of phosphorus in the reactor.

For no phosphorus present in the feed, $y_P=0$ and the asymptotic coking rate then can be expressed as

$$r_a \Big|_{y_P=0} = r_{ab} = k_m C_A^n \quad (6)$$

whereas for $y_P=1$, the surface is completely covered with the complex and

$$r_a \Big|_{y_P=1} = r_{aP} = k_P C_A^n \quad (7)$$

r_{ab} can be determined experimentally from data on a phosphorus-free naphtha. In contrast, r_{aP} cannot be determined experimentally because the concentration of phosphorus at which $y_P \rightarrow 1$ is not known.

From equations (3), (6), and (7), we obtain

$$r_a = r_{aP} y_P + r_{ab} (1-y_P) \quad (8)$$

$$\text{or} \quad \frac{1}{y_P} = \frac{r_{ab}}{r_{ab}-r_a} - \frac{r_{aP}}{r_{ab}-r_a} \quad (9)$$

substituting equation (5) in equation (9) we obtain

TABLE 4: VARIATION OF ASYMPTOTIC RATE OF COKING
WITH TEMPERATURE AND PHOSPHORUS CONCENTRATION

<u>Temperature, K</u>	<u>Phosphorus concen- tration, ppm</u>	<u>Asymptotic rate of coking $\times 10^2$, kg/m²-h</u>
1088	0	8.60
	50	5.12
	100	3.80
	200	2.85
	500	1.64
	1000	0.75
1098	0	11.00
	50	6.62
	100	4.85
	200	3.60
1108	0	13.60
	50	8.60
	100	5.95
	200	4.40

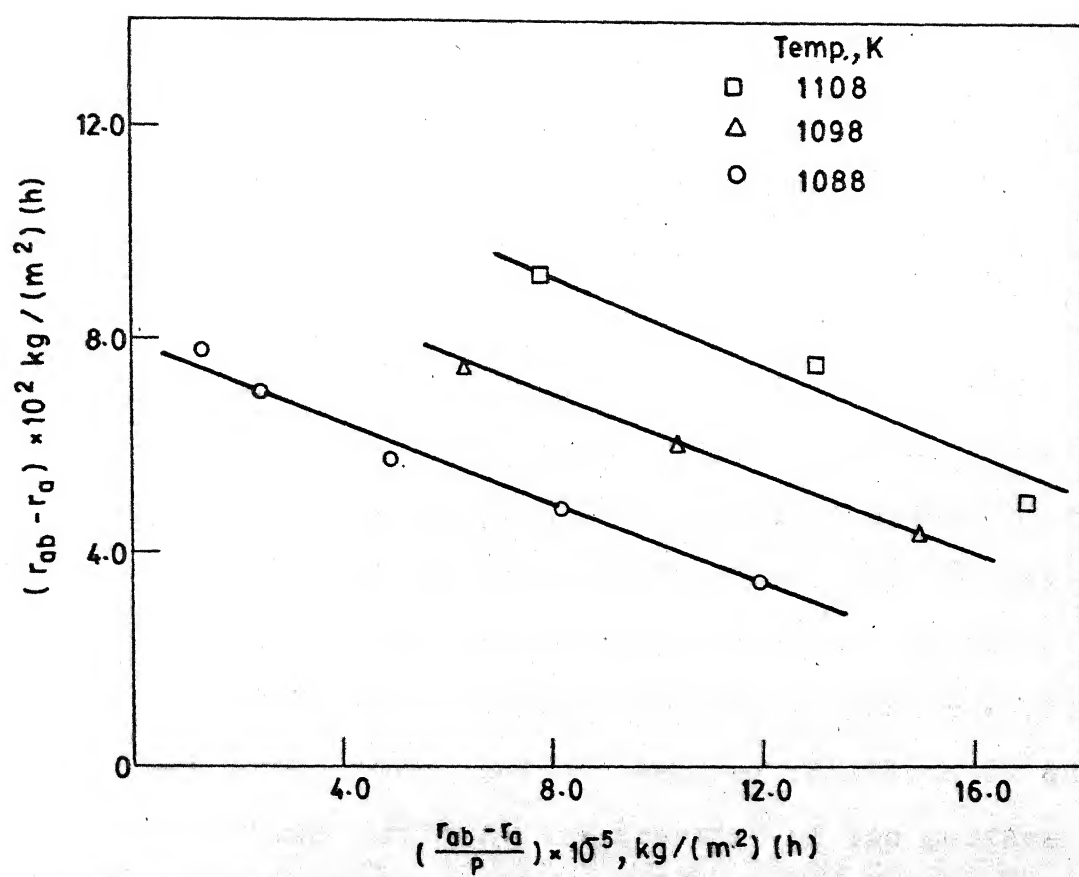


Fig. 14 Determination of r_{ad} and K at different temperatures

$$\frac{r_{ab}}{r_{ab} - r_a} = 1 + \frac{1}{K_P P} + \frac{r_{aP}}{r_{ab} - r_a} \quad (10)$$

or

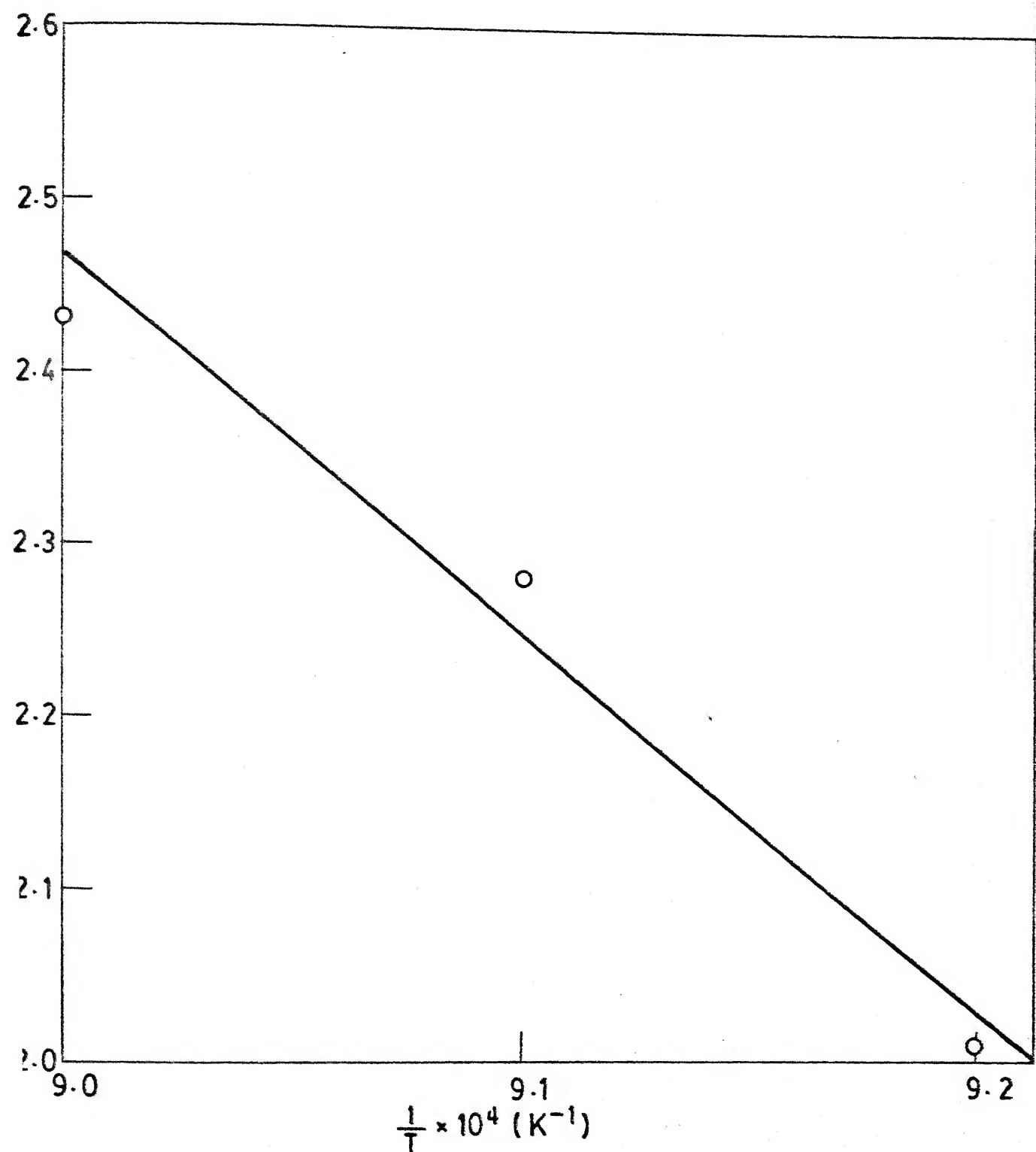
$$(r_{ab} - r_a) = (r_{ab} - r_{aP}) - \frac{1}{K} \left(\frac{r_{ab} - r_a}{P} \right) \quad (11)$$

For a particular temperature, r_{ab} is known from the asymptotic rate of coking at $P=0$ and r_a is known at different concentration of phosphorus. Thus a plot of $(r_{ab} - r_a)$ vs $\left(\frac{r_{ab} - r_a}{P}\right)$ should give a straight line with slope of $(-1/K)$ and an intercept of $(r_{ab} - r_{aP})$.

The asymptotic rate of coke formation at various temperatures and concentration of phosphorus obtained from the data shown in Figs. 6 and 10 are given in Table 4. The plot of $(r_{ab} - r_a)$ vs $\left(\frac{r_{ab} - r_a}{P}\right)$ at these different temperatures is shown in Fig. 14. Considering the simplifying assumptions, the model equation (11) represents the data very satisfactorily for all the runs with sulphur-free naphtha, and the values of K and r_{aP} together with the 95% confidence limits are shown in Table 5. r_{aP} increases whereas K decreases with temperature which shows that the complex formation is an exothermic process and that the fraction of the surface covered with the complex at a constant phosphorus concentration decreases with temperature. The activation energies for k_p , k_m , and K were found to be 175.41 ± 8.5 , 179.38 ± 6.0 and 44.89 ± 5.0 MJ/kmole respectively. Using a phosphorus-free naphtha, the activation energy for coke formation has been reported in the range of 208.6 to 240.3. The lower value in

TABLE 5: VARIATION OF K AND r_{ap} WITH TEMPERATURE

Temperature, K	Equilibrium constant, K	r_{ap} , kg/(m) ² (h)
1088	2.72×10^4	7.45
1098	2.62×10^4	9.97
1108	2.46×10^4	11.35



15 Arrhenius plot for deposition of coke on Inconel 600 with phosphorus complex

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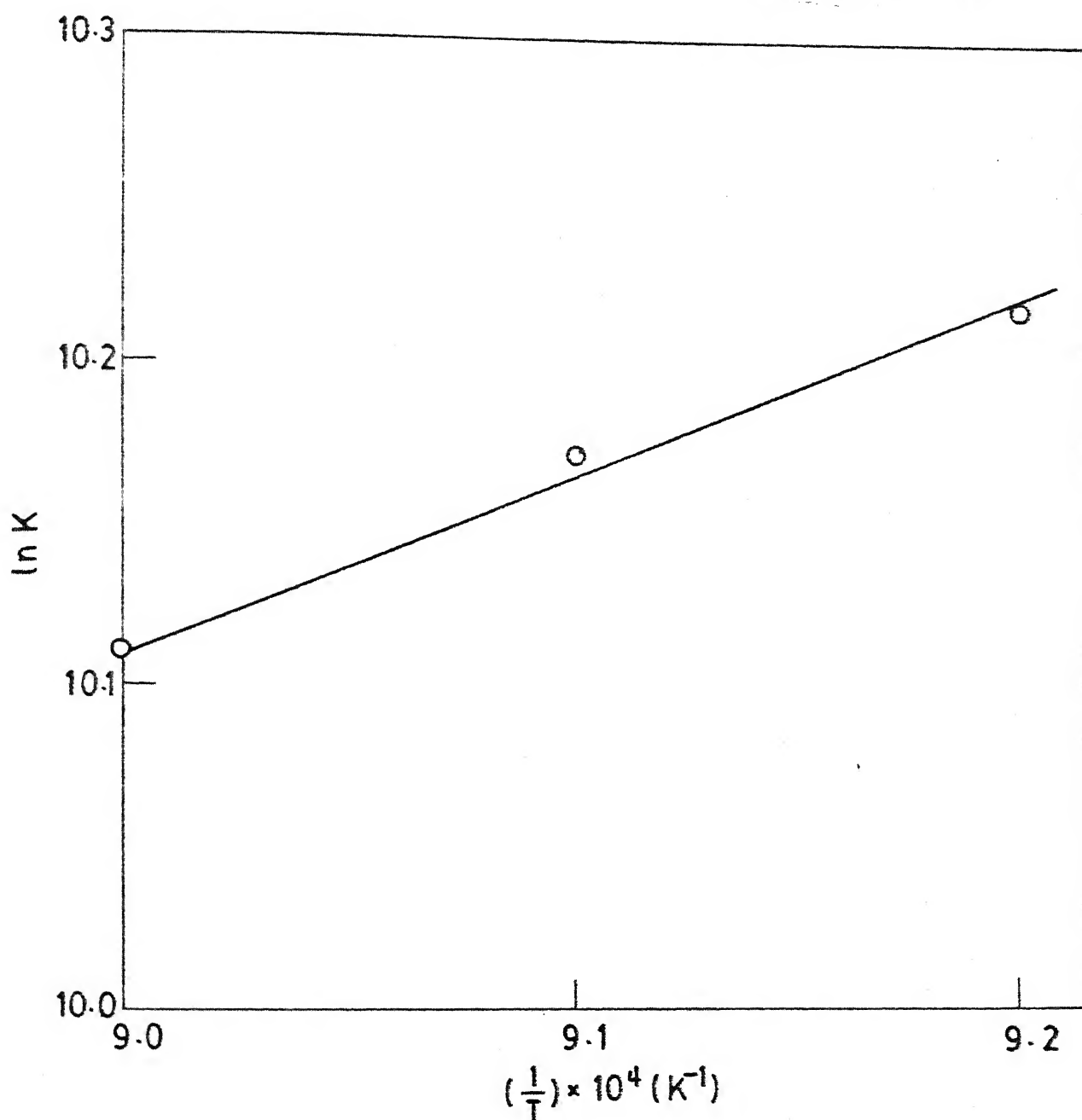


Fig.17 Variation of $\ln K$ vs $\frac{1}{T}$

this study is most probably due to the presence of 50 ppm of sulphur in the earlier studies or the higher aromatic content and boiling point of the feed used in this study.

4.8 Modelling of Coke Formation During Pyrolysis of Naphtha Containing Both Phosphorus and Sulphur:

The above model can be extended to account for a feed containing both phosphorus and sulphur. It will be assumed that the presence of sulphur does not significantly affect the order of the coke formation reaction with respect to aromatic concentration, so that the asymptotic rate of coke formation can be expressed as

$$r_a = k_P y_P C_A^n + k_S y_S C_A^n + (1-y_P-y_S) k_m C_A^n \quad (12)$$

where y_S = fraction of the metal surface covered with metal sulphur complex

k_S = rate constant for coke forming on a surface completely covered with sulphur complex.

Both y_S and k_S depend on temperature.

Extended the analysis given in Section 4.7, we obtain

$$\frac{dy_P}{dt} = k_{f,P} (1-y_P-y_S) P - k_{r,P} y_P \quad (13)$$

and

$$\frac{dy_S}{dt} = k_{f,S} (1 - y_P - y_S) S - k_{r,S} y_S \quad (14)$$

At equilibrium, $\frac{dy_P}{dt} = \frac{dy_S}{dt} = 0$

Thus, we obtain

$$y_P = \frac{K_P P}{1 + K_S S + K_P P} \quad (15)$$

$$\text{and } y_S = \frac{K_S S}{1 + K_S S + K_P P} \quad (16)$$

where

$$K_S = \frac{k_{f,S}}{k_{r,S}} \quad \text{and} \quad K_P = \frac{k_{f,P}}{k_{r,P}}$$

Solving equations (12), (15) and (16), we obtain the expression,

$$K_P A P - (r_a - r_{ab}) K_P P = (r_a - r_{ab}) + K_S (r_a - r_{ab}) S - K_P B S \quad (17)$$

where $A = (r_{ap} - r_{ab})$

$$\text{and } B = (k_S C_A^n - r_{ab}) \frac{K_S}{K_P} \quad (18)$$

In equation (17), for a particular temperature except for B and K_S all other parameters are known. Therefore, from data at two different sulphur and phosphorus concentrations, we can obtain K_S and $k_S C_A^n$. From the values of r_a at $P = 100$, $S = 100$ and $P = 180$, $S = 400$, the values of K_S and $k_S C_A^n$ at 1088 K were found to be 1.1445×10^4 and 6.91×10^{-2} $\text{kg}/(\text{m}^2)(\text{h})$, respectively.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions:

Based on the results of this study, the following conclusions can be made:

Rate of coke deposition during pyrolysis of naphtha can be reduced by coating the reactor walls with sodium silicate. However, the rate of coke formation increases with successive decokings due to gradual loss of sodium silicate from the metal surface.

The reduction of coke deposition on sodium silicate coated surfaces is not due to the catalytic gasification of coke-steam reaction, and steam acts only as an inert.

Addition of triethyl phosphite and thiophene significantly reduces the coking rate by passivating the metal active sites. To maintain a reduced coking rate, continuous injection of the additive is necessary. Addition of phosphorus does not affect the homogeneous reaction during pyrolysis but it does affect the surface reaction, by forming a metal-phosphorus complex in equilibrium with the phosphorus in the gas phase. Addition of phosphorus is more effective than sulphur.

The coke formation can be satisfactorily modelled by assuming that coke is simultaneously depositing at different rates on the surface covered with the phosphorus complex and on the bare surface.

5.2 Recommendation:

The following recommendations are proposed for further study:

The effect of phosphorus on naphtha pyrolysis should be checked further by analysing in detail the liquid and gaseous products.

The effect of different types of phosphorus compounds on the rate of coke formation should be investigated.

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APPENDIXRates of Coke Formation with Run Time at Different Temperatures and Concentrations of Phosphorus (ppm)

1. Temperature = 1098 K, $\delta = 0.70 \frac{\text{Kg steam}}{\text{Kg naphtha}}$, $\tau = 0.53 \text{ s}$

Phosphorus concentration, ppm	Run time, R	Rate of coke formation kg/(m ²)(h)
0	0.5	15.2
	1.0	14.5
	1.5	13.2
	2.0	12.4
	2.5	11.6
	3.0	11.3
	3.5	10.9
	4.0	11.0
	4.5	11.0
	5.0	10.9
50	0.5	8.2
	1.0	7.5
	1.5	7.8
	2.0	7.0
	2.5	6.8
	3.0	6.6
	3.5	6.2
	4.0	6.4
	4.5	6.8
	5.0	6.6

100	0.5	7.7
	1.0	7.1
	1.5	6.5
	2.0	5.5
	2.5	5.3
	3.0	4.9
	4.0	4.7
	4.5	4.7
	5.0	4.9
200	0.5	7.3
	1.0	5.0
	1.5	5.0
	2.0	4.6
	2.5	4.4
	3.0	3.7
	3.5	3.6
	4.0	3.4
	4.5	3.8
	5.0	3.3

2. Temperature = 1108 K, $\delta = 0.70 \frac{\text{kg steam}}{\text{kg naphtha}}$, $\tau = 0.53 \text{ s}$

Phosphorus concentration, ppm	Run time, h	Rate of coke formation $\times 10^2 \text{ kg}/(\text{m}^2)(\text{h})$
0	0.5	16.4
	1.0	15.8
	1.5	15.0
	2.0	14.7
	2.5	14.3

50

3.5	13.3
4.0	13.2
4.5	13.5
5.0	13.5
0.5	10.0
1.0	9.1
1.5	9.2
2.0	9.1
2.5	8.8
3.0	8.9
3.5	8.7
4.0	8.9
4.5	8.2
5.0	8.6
0.5	8.9
1.0	8.5
1.5	7.5
2.0	6.7
2.5	6.4
3.0	6.0
3.5	5.9
4.0	5.9
4.5	6.0
5.0	5.9

100

200

0.5

7.9

1.0

7.1

1.5

5.1

2.0

5.2

2.5

5.0

3.0

4.6

3.5

4.4

4.0

4.1

4.5

4.4

5.0

4.6